

Uranium(VI) Sorption to Sediments Under High pH and Ionic Strength Conditions

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Summary

A number of potential sources for uranium pollution have background chemistries of high ionic strengths (>0.5 M) and pH (>10), including the liquids from many storage tanks and leachates from vitrified-, saltstone-, and grout-waste forms. The effect of these background chemical conditions on the tendency of U(VI) to sorb to natural sediments is unknown. To evaluate these factors, a series of batch-type experiments were conducted to determine the effects of U(VI) concentration, pH, and ionic strength on U(VI) sorption to a natural sediment containing carbonate mineral phases. The results show that U(VI) adsorption remained constant between 3.3 and 100 $\mu\text{g/L}$ UO_2^{2+} at pH 8.3 and ionic strength of 0.02 M, suggesting that the simple distribution coefficient (K_d) model could be used to describe adsorption between this concentration range. Uranium(VI)- K_d and solubility values did not change as the ionic strength was increased with NaClO_4 to 14 mM. Uranium(VI)- K_d values essentially doubled from 1.07 to 2.22 mL/g as the pH of the system increased from pH 8.3 to 9.3. Above pH 10.3, precipitation of U(VI)-containing solids occurred, resulting in apparent K_d values of >400 mL/g. Precipitation did not occur unless a sediment was present. This suggests that heterogeneous precipitation occurred. Thus, in carbonate systems with a pH greater than about 10.5, U(VI) mobility may be much less than in near-neutral pH systems. These results have important ramifications for performance- and risk-assessment calculations involving the transport of U(VI) from highly alkaline sources.

Introduction

A number of potential sources for uranium pollution into the environment have background chemistries of high ionic strengths and pH, including the liquids from many storage tanks and leachates from vitrified-, saltstone-, and grout-waste forms. These sources originated primarily from the legacy of nuclear material production and spent fuel storage. Radionuclide tank waste is commonly maintained at pH levels >10.5 to minimize structural corrosion. The waste volume in these tanks is typically minimized by evaporating large volumes of water, resulting in high ionic strength liquors, typically >1 M. It is anticipated that most tank waste will be converted to vitrified-, grout-, or saltstone-waste forms for eventual storage or disposal. Leachate plumes emanating from these waste forms are also expected to have high ionic strengths and pH levels. The effect of high ionic strength and pH on the

tendency of dissolved uranium to sorb to sediments is not known. This lack of knowledge could adversely affect performance- and risk-assessment modeling of tank and disposal facilities by increasing the uncertainty and requiring unrealistically conservative estimates be used as input parameters.

pH has been shown to have a large effect on U(VI) adsorption tendencies to pure mineral phases [1, 2] and natural sediments [3, 4]. These studies indicate that a common trend for U(VI) adsorption is that it increases from pH 3.5 to about 8, remains constant until about pH 8.5, and then decreases at pH >9 . The cause for the increase in adsorption between pH 3.5 to 8 is due to the overall increase in the number of adsorption sites (specifically, increases in the negative charge on the variable charged clays). The decline in U(VI) adsorption at pH >9 has been attributed to the formation of anionic carbonate and hydroxyl complexes in solution, such as $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$, $\text{UO}_2(\text{CO}_3)_2^{2-}$, $\text{UO}_2(\text{CO}_3)_3^{4-}$, and $\text{UO}_2(\text{OH})_3^-$. These anionic uranyl complexes have been shown to adsorb to mineral surfaces [2], however, the extent that they adsorb may be less than the cationic uranyl species present at the lower pH values.

Elevated solution ionic strength, or salt concentration, has been shown to have significant effects on sorption processes [5, 6]. Generally, as the ionic strength increases, adsorption of cationic and anionic contaminants decreases because there is greater competition for adsorption sites and the activity of the sorbed species decreases. However, high ionic strengths can occasionally have the opposite effect, that is, as the ionic strength increases, solutes associate with the solid phase also increases [5]. The cause for this has been attributed to precipitation and/or coprecipitation.

The objective of this study was to determine the effects of high pH and ionic strength on U(VI) sorption to a carbonate-containing sediment. Carbonate-containing sediments are common throughout western United States. In addition to providing sorption sites, carbonates also maintain high concentrations of carbonates (CO_3^{2-} and HCO_3^-) in the aqueous phase, thereby greatly influencing dissolved U(VI) speciation. A series of batch experiments was conducted to simulate various environmental conditions of a U(VI) plume emanating from alkaline, uranium waste source. Information from these experiments were to be used

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Table 1. Chemical composition of uncontaminated groundwater (<0.45- μ m filter) used in these studies

Constituent	Concentration (mg/L)
pH	8.4 (unitless)
Cl ⁻	24
NO ₃ ⁻	1.7
SO ₄ ⁻	109
Total organic C	0.73
Total alkalinity (as CO ₃ ⁻)	160
Al	0.14
B	0.05
Ba	0.069
Ca	58
Fe	3
K	14
Mg	16
Mn	0.046
Na	30
Si	16.2
U(VI) as UO ₂ ⁺	0.005

to provide a conceptual model for U(VI) geochemistry at the proposed Immobilized Low-Activity Waste site at the Hanford Site in Richland, Washington, United States.

Materials and methods

General procedure for sorption experiments

Four experiments were conducted to evaluate the effects of various aqueous parameters on U(VI) sorption to sediments containing carbonates. The experiments were entitled U(VI) Concentration Experiment, Ionic Strength Experiment, Nonstabilized pH Experiment, and Stabilized pH Experiment. The general procedure used in all these experiments was essentially identical except that one parameter was systematically changed.

Groundwater collected from a well located in an uncontaminated portion of the Hanford Site in Richland, Washington (Well S3-25) was used as the aqueous phase in all experiments (Table 1). The groundwater was analyzed using standard techniques. Uranium(VI) was measured by laser phosphorimetry (Chemchek Instruments, Inc., [7]). All U(VI) results were reported in terms of UO₂⁺ concentrations. Thus, the UO₂⁺ concentration data includes both free-ion and complex species of UO₂⁺. The laser phosphorimetry method had a detection limit 0.5 μ g/L UO₂⁺ and analytical precision of 2% at 10 μ g/L UO₂⁺. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was used to determine dissolved cation concentrations and it had an analytical precision of $\leq \pm 4\%$ at 5 mg/L. Ion chromatography (IC) was used to determine dissolved anion concentrations and it had an analytical precision of $\leq \pm 4\%$ at 5 mg/L.

The two sediments used in these studies were collected from the side walls of two trenches (AE-3 and 94) located in the 200 Area on the Hanford Site (Table 2). Both sediments were collected at a depth of

approximately 10 m. They were selected because they have different textures. Sediment characterization was conducted using standard methods: cation exchange capacity was determined by the Na⁺-exchange ion method [8], N₂ by the BET method [9], particle size distribution by the pipette method [10], particle density by the submersion method [11], hydraulic conductivity by the constant head method [12], carbonate concentration by acid neutralization of the carbonate, followed by back titration of the excess acid [13], pH by the 1:1 solid:solution method [14], and mineralogy by X-ray diffraction [15].

Trench AE-3 sediment has a texture of a silty loam and the Trench-94 sediment has a texture of a very coarse sand. The mineralogy of the clay-size fraction of the Trench AE-3 sediment was dominated by smectite, illite, and vermiculite, whereas the clay-fraction in the Trench-94 sediment was dominated by smectite, plagioclase, and illite. X-ray diffraction analysis of the samples revealed that the carbonate phase was dominated by calcite. The hydrous iron oxide concentration of these sediments were not measured but based on measurements made on nearby sediments, they likely contained between 0.2 to 0.5% [wt] Fe₂O₃ [16].

The experiments were not conducted in a CO₂-free chamber in an attempt to simulate actual conditions in a subsurface environment. The sediment was first preequilibrated with groundwater. This was accomplished by adding groundwater to the sediments, shaking the suspensions overnight, centrifuging, pouring off the supernatant, and then measuring the pH of the supernatant. This was repeated until the pH of the groundwater did not change before and after contact with the sediment, usually three washes. The purpose of this preequilibration step is to isolate the radionuclide adsorption reaction from the large number of other reactions that may occur while sediments and aqueous solutions come to chemical equilibrium. This has been shown to be a critical step for accurately measuring adsorption values and minimizing precipitation and/or coprecipitation of several radiotracers [6].

Uranium(VI) solutions were made by adding the appropriate amount of UO₂(NO₃)₂ to groundwater (Table 1) and then the solutions were placed on a platform shaker for 7 days, a period selected to insure that steady state conditions were achieved. These solutions were then passed through a 0.007- μ m filter and then the filtrates were analyzed for pH, electrical conductivity, and total dissolved U(VI).

An index of the solubility of U(VI) in the various treatment solutions was estimated by the filtration ratio:

$$\text{Filtration ratio} = \frac{[\text{U(VI)}]_{\text{final}}}{[\text{U(VI)}]_{\text{initial}}} \quad (1)$$

where $[\text{U(VI)}]_{\text{final}}$ is the U(VI) concentration in the <0.007- μ m filtrate and $[\text{U(VI)}]_{\text{initial}}$ is the U(VI) concentration added to the groundwater. No sediment was added to the solutions used to calculate the filtration ratios.

Table 2. Selected properties of the sediments used in these studies

Constituent	Trench AE-3	Trench-94
Texture	Silty loam	Very coarse sand
pH	8.3	8.2
CEC (meq/100 g)	6.4	5.3
Surface area (m ² /g)	14.8	6.3
<i>In situ</i> gravel (% wt) ^a	<1	32.7
<i>In situ</i> sand (% wt)	41	67
<i>In situ</i> silt (% wt)	50	0.26
<i>In situ</i> clay (% wt)	9	0.04
<2-mm sand (% wt) ^b	41	99.55
<2-mm silt (% wt)	50	0.39
<2-mm clay (% wt)	9	0.06
Particle density (g/cm ³)	2.74	2.84
Saturated hydraulic conductivity (cm/s)	6e-6	—
CaCO ₃ (% wt)	1.92	1.77
Dominant mineral in clay fraction	Smectite (57%) Illite (19%) Vermic. (14%)	Smectite (38%) Plagioclase (26%) Illite (13%)

^a *In situ* compositions refer to the total sediment as it exists in the ground. This sediment was not used in the adsorption experiments.

^b The <2-mm fraction was used in the adsorption experiments.

A 20-mL aliquot of the filtered U(VI) solutions was then added to 10-g of preequilibrated sediment. The U(VI)/groundwater/sediment suspensions were placed on a slow-moving platform shaker for 14 or 30 days. This duration was selected to insure that the system was in a steady state. Preliminary experiments showed that uranium sorption to these sediments remained constant between 2 and 30 days [16]. The suspensions were centrifuged and the supernates were then passed through 0.45- μ m filters. This filter size was used instead of a 0.007- μ m filter because the latter would clog with the soil suspension. The U(VI), pH, and electrical conductivity of the filtrates were measured.

The distribution coefficients (K_d ; mL/g) were calculated using Eq. (2):

$$K_d = \frac{(C_{\text{spike}} \times V_{\text{spike}}) - C_{\text{equil.}}(V_{\text{spike}} + V_{\text{excess}})}{C_{\text{final}} \times M_{\text{sed}}} \quad (2)$$

where V_{excess} (mL) is the volume of excess solution left after the third preequilibration wash (weight of excess solution divided by solution density), M_{sed} is the sediment mass (g), V_{spike} is the volume of U(VI) solution (mL), C_{final} is the U(VI) concentration in the effluent solution after equilibration (μ g/L), and C_{spike} is the initial U(VI) concentration in the spike solution (μ g/L; positive control).

A sediment-to-solution ratio of 1:2 was used in these tests. This high ratio was used to improve K_d measurement accuracy. As can be seen from Eq. (2), the concentration of adsorbed U(VI) is determined by subtracting the concentration of the U(VI) in solution before, C_{spike} , and after, C_{final} , contact with the sediment. If little adsorption takes place, then the difference between C_{spike} and C_{final} will be small. Compounding this issue is that detection accuracy of the laser-phosphorimetry method improves at higher concentrations. Thus, one of the difficulties in determining

low K_d values is that two large numbers must be subtracted from each other to determine a small value, a poorly poised mathematical situation. To obtain a greater difference between C_{spike} and C_{final} , the ratio of sediment to solution was increased in these tests.

Three replicates of each treatment were made. Two types of control treatments conducted as part of these experiments: a negative and a positive control. The positive control containing the U(VI)-spiked groundwater and no sediment served to account for U(VI) sorption to labware and filters. The negative control contained sediment and groundwater without U(VI). It served to account for background U(VI) in the uncontaminated sediment and groundwater and to provide information about U(VI) detection interferences during laser phosphorimetry.

Uranium(VI) concentration experiment

Uranium(VI)- K_d values were determined as a function of dissolved U(VI) concentrations following the procedure described above. Uranium nitrate was added to uncontaminated groundwater (Table 1) to make initial concentrations of solution U(VI) ranged from 3.3 to 100 μ g/L UO_2^{2+} . The resulting solutions were mixed with the Trench 94 sediments (Tables 2). The U(VI) solutions and sediment suspensions were placed on a platform shaker for 30 days. The suspensions were then passed through a 0.45- μ m filter and the filtrate analyzed for U(VI) concentration by laser-phosphorimetry.

Ionic strength experiment

The effect of solution ionic strength on the solubility [filtration index, Eq. (1)] and K_d values of U(VI) was evaluated by varying the amount of sodium perchlor-

ate (NaClO_4) added to groundwater/sediment suspensions. Sodium perchlorate was selected as the salt to vary ionic strength because sodium will likely be the dominant cation emanating from most waste forms and the perchlorate anion (ClO_4^-) is a non-complexing ligand. Thus, the perchlorate anion will increase the ionic strength without greatly affecting the chemical speciation. Sodium perchlorate was mixed with groundwater to make 0, 0.3, 1.0, 1.7, 4.1, and 14.0 mM solutions. These solutions were placed on a platform shaker to equilibrate overnight. Then a concentrated uranium nitrate stock solution was added to these solutions to make a final U(VI) concentration of $\sim 190 \mu\text{g/L}$. The U(VI)-sodium perchlorate groundwater solutions were permitted to equilibrate for 7 days. These solutions were then used in sediment-sorption experiments using the general procedure for sorption experiments described above.

Nonstabilized pH experiment

Two studies were conducted in which sodium hydroxide (NaOH) was used to vary the pH of Trench AE-3 sediment/groundwater suspensions. In the Nonstabilized pH Experiment, a set amount of NaOH was added to a groundwater. The sediment was preequilibrated with groundwater and not the NaOH -amended solutions. The sediments were equilibrated in this manner to simulate conditions at the edge of the U(VI) contaminant plume. In the second study, the Stabilized pH Experiment, the groundwater and sediment was titrated and "equilibrated" to preestablished pH levels using NaOH . The sediments were equilibrated in this manner to simulate conditions within a large plume. Sodium hydroxide was selected for these studies because the Na^+ cation and OH^- anion are the dominant ions leached from several types of glass and grout waste forms.

In the Nonstabilized pH Experiment, NaOH -amended groundwater solutions were made with identical molar-concentration additions as were used in the Ionic Strength Experiment, 0, 0.3, 1.0, 1.7, 4.1, and 14 mM. The intent was to create experimental conditions for making comparisons between the results from the two experiments. The pH and the ionic strength was concomitantly varied in the Nonstabilized pH Experiment, whereas only the ionic strength was varied in the Ionic Strength Experiment. After equilibrating for 7 days, the NaOH groundwater solutions were spiked with $\sim 190 \mu\text{g/L}$ UO_2^{2+} . The U(VI) solutions were then permitted to equilibrate for another 7 days, after which they were passed through a $0.007\text{-}\mu\text{m}$ filter. These solutions were then used in sediment-sorption experiments using the general procedure for sorption experiments described above.

Stabilized pH experiment

The pH values of six groundwater suspensions were adjusted with NaOH to pH values ranging from 8.29

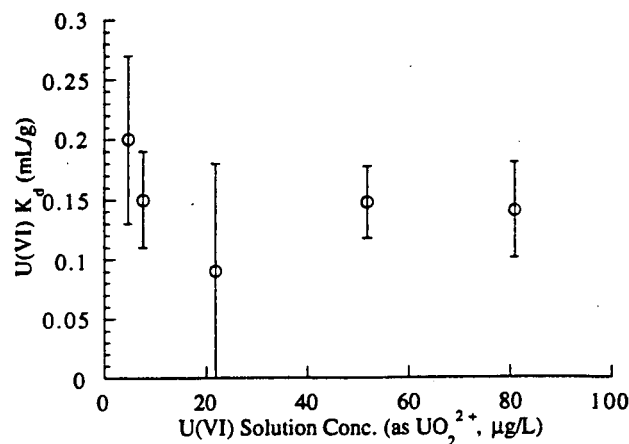


Fig. 1. U(VI)- K_d values as a function of solution U(VI) concentrations (contact time = 30 days; sediments = Trench 94; sediment:solution = 1:2; solution = uncontaminated groundwater).

to 12.01. Once the pH values remained stable ($\text{pH} \pm 0.2$) for a period of about 7 days, the solutions were spiked with $\sim 190 \mu\text{g/L}$ UO_2^{2+} and then equilibrated for another 7 days. The solutions were then passed through a $0.007\text{-}\mu\text{m}$ filter, and the pH and U(VI) concentrations of the filtrate were determined. These solutions were then used in sediment-sorption experiments using the general procedure for sorption experiments described above.

Results and discussion

Uranium(VI) concentration experiment

The U(VI)- K_d values for a given sediment were quite similar throughout the 3.3 to $100 \mu\text{g/L}$ UO_2^{2+} range investigated (Fig. 1). The average K_d for the Trench 94 sediment was $0.14 \pm 0.07 \text{ mL/g}$. The fact that adsorption was relatively constant over this range is indicative that the K_d construct is appropriate for these conditions. More complicated and robust models, such as the Langmuir or Freundlich model, are not needed to describe these data for these specific geochemical conditions. This is not surprising considering that the number of U(VI) adsorption sites in these sediments likely far exceeds the low range of U(VI) concentrations used in these studies.

Ionic strength experiment

Electrical conductivity is an indirect measure of the ion activity (concentration) in solution. The electrical conductivity increased linearly with amount of sodium perchlorate (NaClO_4) added to the groundwater solution (Table 3). This suggests that the Na^+ and ClO_4^- ions went into solution and did not form any complex species. The sodium perchlorate had no significant effect on the final concentration of U(VI) following adsorption reactions (Table 3). Uranium(VI) concentrations in the six spiked solutions average $196 \pm 3 \mu\text{g/L}$.

Table 3. Uranium(VI) filtration ratios of groundwater treated with varying concentrations of sodium perchlorate: Ionic Strength Experiment^a

Final concentration of NaClO ₄ added (mM)	Electrical conductivity (μS/cm)	Final U(VI) in <0.007-μm filtrate (μg/L UO ₂ ²⁺)	Filtration ratio ^b (unitless)
0	565±0	192±7	1.00±0.04
0.3	594±0	195±2	1.02±0.01
1.0	661±0	197±2	1.03±0.01
1.7	742±0	194±4	1.01±0.02
4.1	967±0	201±4	1.05±0.02
14.0	1984±0	197±4	1.02±0.02

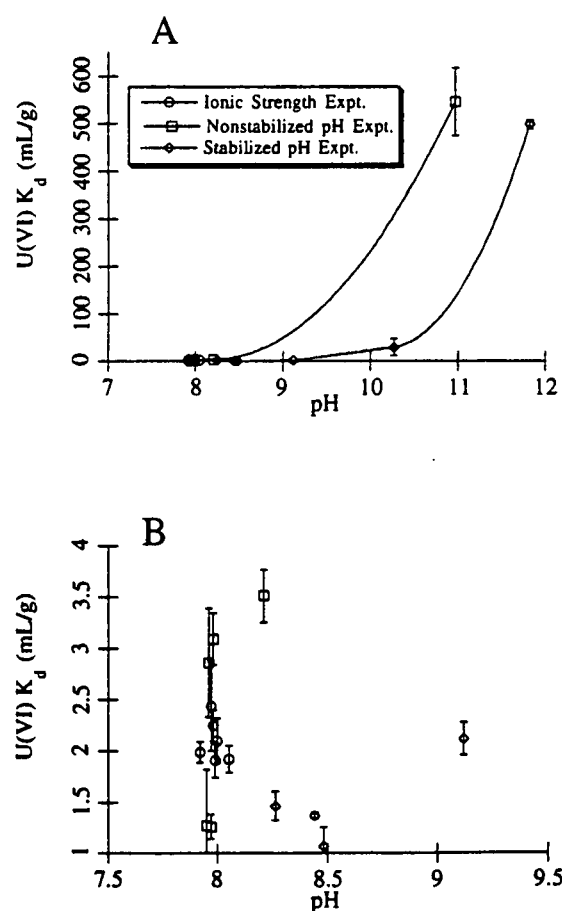
^a Means followed by standard deviation of three observations; Trench AE-3 sediment; initial U(VI) concentration ~192 μg/L UO₂²⁺; equilibration period for NaClO₄ adjustment = 14 days; equilibration period for subsequent U(VI) spike = 14 days.

^b The filtration ratio is defined in Eq. (1).

Table 4. Effects of sodium perchlorate additions on U(VI)-K_d values: Ionic Strength Experiment^a

NaClO ₄ added (mM)	Suspension pH after 1-hr contact time	Final suspension pH after 14-day contact time	K _d (mL/g)
0	8.31±0.00	7.92±0.02	1.99±0.10
0.3	8.37±0.01	8.05±0.01	1.92±0.13
1.0	8.30±0.01	7.99±0.00	1.91±0.17
1.7	8.32±0.03	7.99±0.01	2.10±0.22
4.1	8.26±0.01	7.98±0.00	2.25±0.15
14.0	8.27±0.01	7.97±0.01	2.44±0.44

^a Mean and standard deviation of three observations. Trench AE-3 sediment; groundwater was spiked with ~190 μg/L UO₂²⁺.

**Fig. 2.** U(VI)-K_d values as a function of pH for all three experiments (A) for the entire data set, and (B) between pH 7.5 and 9.5.

The NaClO₄-amended solutions described in Table 3 were used in U(VI) sorption experiments. There was no statistically significant ($P \geq 0.05$) correlation between U(VI)-K_d values and the amount of added sodium perchlorate (Table 4, Fig. 2). It is important to note that the final pH values of the six NaClO₄-amended solutions after the 14-day contact time were essentially identical, indicating that ionic strength increased independently of pH in these experiments.

Nonstabilized pH experiment

The pH of the NaOH-amended groundwater solutions ranged from 8.54 to 11.88 (Table 5). The filtration ratios decreased consistently and significantly ($P \leq 0.05$) from 1.00 to 0.92, i.e., 8% of the U(VI) in the highest pH solution could not pass through the 0.007-μm filter and all of the U(VI) in the lowest pH solution passed through the 0.007-μm filter. The cause for this small decrease in the filtration index is not known. Calculations of the saturation indices suggested that uranium phases did not precipitate from these solution (i.e., the saturation indices were <0). As expected, the solution electrical conductivity levels increased concomitantly with the amount of NaOH added. The changes observed in the filtration ratios in this study can be attributed primarily to the increase in NaOH (or pH) and not the increase in electrolyte concentrations because similar increases of ionic strength in the Ionic Strength Experiment did not influence filtration ratios (Table 3).

The U(VI) solutions described in Table 5 were mixed Trench AE-3 sediment. By the end of the 14-

Table 5. Uranium(VI) filtration ratios of groundwater treated with varying concentrations of sodium hydroxide: Nonstabilized pH Experiment*

Final concentration of NaOH added (mM)	pH	Electrical conductivity ($\mu\text{S}/\text{cm}$)	Final U(VI) in $<0.007\text{-}\mu\text{m}$ filtrate ($\mu\text{g}/\text{L UO}_2^{2+}$)	Filtration ratio ^b (unitless)
0	8.59	533 \pm 0	195 \pm 4	1.00 \pm 0.02
0.3	8.54	504 \pm 0	188 \pm 4	0.96 \pm 0.02
1.0	8.64	479 \pm 0	185 \pm 4	0.95 \pm 0.02
1.7	9.52	480 \pm 0	182 \pm 5	0.93 \pm 0.03
4.1	10.41	623 \pm 0	184 \pm 3	0.94 \pm 0.01
14.0	11.88	2740 \pm 0	179 \pm 7	0.92 \pm 0.04

* Trench AE-3 sediment; equilibration period for NaOH adjustment = 14 days; equilibration period for subsequent U(VI) spike = 7 days.

^b The filtration ratio is defined in Eq. (1).

Table 6. Effect of sodium hydroxide additions on U(VI)- K_d values: Nonstabilized pH Experiment*

NaOH added (mM)	Suspension pH after 1-hr contact time	Final suspension pH after 14-day contact time	K_d (mL/g)
0	8.13 \pm 0.05	7.97 \pm 0.00	1.26 \pm 0.12
0.3	8.15 \pm 0.01	7.95 \pm 0.03	1.27 \pm 0.55
1.0	8.17 \pm 0.01	7.96 \pm 0.02	2.86 \pm 0.53
1.7	8.38 \pm 0.01	7.98 \pm 0.07	3.09 \pm 0.25
4.1	9.34 \pm 0.01	8.21 \pm 0.07	3.51 \pm 0.26
14.0	11.56 \pm 0.00	10.97 \pm 0.07	545.7 \pm 70.4

* Mean and standard deviation of three observations; Trench AE-3 sediment; groundwater amended with $\sim 190 \mu\text{g}/\text{L U(VI)}$ (as UO_2^{2+}).

day equilibration period, the pH had decreased between 0.1 and 0.5 pH units, indicating that equilibrium conditions had not been achieved (Table 6). This was not surprising because these sediments were not preequilibrated with the appropriate NaOH-amended solutions. The U(VI)- K_d values gradually increased from 1.26 to 3.51 mL/g as the amount of NaOH added increased between 0 and 4.1 mM (Table 6 and Fig. 2). This trend, which occurred between the narrow pH range of 7.95 to 8.21, may be attributed to different fundamental sorption processes. As the pH increased, the number of surface hydroxyl groups on the iron oxides became increasingly more negative, thereby increasing the number of surface complexation sites for cationic uranium sorption [2, 17]. Another mechanism by which U(VI) sorption may have increased as a result of increased pH may be attributed to the variable charge character of the calcite in the sediment [18, 19]. The potential determining ions of calcite are Ca^{2+} and CO_3^{2-} . The point-of-zero charge (PZC) of calcite has been reported to be $\text{pCa} = 4.4$ [20] with the surface exhibiting positive charge at Ca concentration above this value and negative charge at Ca concentration below this value. Based on this PZC, Zachara *et al.* [19] calculated that calcite would carry a predominately positive charge below pH 9.0 in saturated calcium carbonate solutions in contact with atmospheric $\text{CO}_2(\text{g})$ ($\text{pCO}_2(\text{g}) = 3.5$, where CO_2 pressure is in atm). Importantly, pH, or more specifically H^+ and OH^- ion activity, has only an indirect effect on the surface

charge of calcite. Studies, using a streaming potential method, indicate that Ca^{2+} and CO_3^{2-} alone are the dominant surface species and that other solution species, including H^+ and OH^- , have no significant effect on the surface charge [21].

The U(VI)- K_d value for the next higher NaOH treatment, 14-mM NaOH, increased dramatically to 545.7 mL/g (Table 6 and Fig. 2). This pH- K_d trend suggests that the U(VI) sorption mechanism for the highest NaOH treatment may be attributed primarily to precipitation and/or coprecipitation and not adsorption processes. By comparing the U(VI) concentration data for the 14-mM NaOH treatments before (Table 5) and after (Tables 6) contact with sediment, it can be seen that the precipitation did not occur until the sediment was added. The possible phases that may have precipitated will be discussed below.

The addition of NaOH increased the ionic strength as well as the pH of the solutions (Table 5). To evaluate whether the differences in U(VI)- K_d values observed in Table 6 were attributed to pH or ionic strength effects, comparison between the results of the Ionic Strength and Nonstabilized pH experiments can be made (Tables 4 and 6). The molar additions of salts were identical in both experiments; however, in the Ionic Strength Experiment, the pH remained essentially constant, while the ionic strength increased (Tables 3). The U(VI)- K_d values in the Ionic Strength Experiment remained quite similar throughout the entire ionic strength ranged investigated. Thus, the dif-

Table 7. Uranium(VI) filtration ratios of groundwater treated with varying concentrations of sodium hydroxide: Stabilized pH Experiment*

Treatment	pH _{Solution} ^b	Final U(VI) in <0.007- μ m filtrate (μ g/L UO_2^{2+})	Filtration ratio ^c (unitless)
1	8.29 \pm 0.03	179 \pm 3	1.03 \pm 0.02
2	9.00 \pm 0.01	176 \pm 3	0.98 \pm 0.02
3	9.5 \pm 0.02	176 \pm 2	0.98 \pm 0.01
4	10.02 \pm 0.02	176 \pm 4	0.98 \pm 0.02
5	11.00 \pm 0.02	161 \pm 4	0.90 \pm 0.02
6	12.01 \pm 0.01	180 \pm 3	1.00 \pm 0.02
(-) Control ^d	8.32 \pm 0.07	6 \pm 1	—

* Trench AE-3 sediment; equilibration period for sodium hydroxide adjustment = 14 days; equilibration period for subsequent U(VI) spike = 7 days.

^b pH of solution, without sediment, taken at the end of the experiment.

^c The filtration ratio is defined in Eq. (1).

^d No sediment + no U(VI) spike.

Table 8. Effect of sodium hydroxide additions on U(VI)- K_d values: Stabilized pH Experiment*

Treatment	Suspension pH after 5-day contact time	Suspension pH after 14-day contact time	K_d (mL/g)
1	8.17 \pm 0.14	8.48 \pm 0.06	1.07 \pm 0.19
2	8.40 \pm 0.07	8.26 \pm 0.04	1.46 \pm 0.14
3	8.72 \pm 0.03	8.44 \pm 0.03	1.37 \pm 0.03
4	9.31 \pm 0.03	9.12 \pm 0.01	2.12 \pm 0.16
5	10.34 \pm 0.14	10.27 \pm 0.14	29.39 \pm 18.04
6	11.78 \pm 0.08	11.82 \pm 0.07	496.6 \pm 8.8
(+) Control ^b	8.71 \pm 0.57	8.65 \pm 0.15	—
(-) Control ^c	8.32 \pm 0.07	8.29 \pm 0.16	—

* Mean and standard deviation of three observations; Trench AE-3 sediment; groundwater was spiked with $\sim 190 \mu\text{g/L}$ UO_2^{2+} .

^b No sediment + U(VI) spike.

^c No sediment + no U(VI) spike.

ferences in K_d value observed in the Nonstabilized pH Experiment are likely attributed pH and not ionic strength effects.

Stabilized pH experiment

The filtration ratio data in this experiment showed that little U(VI) precipitation occurred prior to adding the sediment (except possibly for Treatment 5) (Table 7). In the Nonstable pH Experiment, the U(VI) filtration ratio slightly decreased as the pH increased (Table 5). The cause for this slight difference between experiment is not known, but may be due in part to experimental variability.

The U(VI)- K_d values increase slightly between the final pH values of 8.48 and 9.12, that is, between Treatments 1 through 4 (Table 8). As discussed above, this trend may be attributed to an increase in the number of adsorption sites or to changes in U(VI) speciation induced by elevating the pH. The U(VI)- K_d value for the two highest pH treatments, Treatments 5 and 6, increased dramatically. This pH- K_d trend, suggests that the sorption mechanism for the two highest pH treatments is likely precipitation and/or coprecipitation and not adsorption.

Precipitation and/or coprecipitation of U(VI) phases

It is important to note that U(VI) precipitation in Treatments 5 and 6 in the Stabilized pH Experiment did not occur for the most part until the solutions were combined with the sediments. In Table 7, the filtration ratio of Treatments 5 and 6 were ≥ 0.9 , indicating that little precipitation of U(VI) occurred in solution. However, once sediments were added to these solutions, precipitation and/or coprecipitation appeared to occur (Table 8). This type of precipitation is referred to as heterogeneous precipitation or heterogeneous nucleation [5, 22, 23]. The term "heterogeneous" refers to the presence of more than one phase in the system. Heterogeneous precipitation is the predominant formation process for solid phases in natural waters [22, 23] because solid surfaces act as catalysts to reduce the activation energy of the precipitation reactions. Qualitatively, if the surface of the solid substrate matches that of the precipitating solid phases, the interfacial energy between the two solids is smaller than the interfacial energy between the solid and the solution. These conditions will promote nucleation at a lower saturation index on the solid substrate surface than in solution.

Table 9. Aqueous chemical composition (mg/L) of groundwater solutions spiked with U(VI) before equilibration with Trench AE-3 sediment: Stabilized pH Experiment

	Treatment 1 ^a	Treatment 5	Treatment 6
pH _{sol'n} ^b	8.3	11.0	12.0
UO ₂ ²⁺	0.185	0.161	0.180
Cl ⁻	24	30	29
SO ₄ ²⁻	109	107	108
PO ₄ ³⁻	1.9	1.3	1.3
CO ₃ ²⁻	160	192	376
Ca	58	2.3	1.3
K	14	20	16
Mg	16	2.0	0.1
Na	30	158	423
H ₄ SiO ₄ ⁰	54	26	29

^a Treatments are numbered in order of the increasing amounts of NaOH added to groundwater. Treatment 1 did not receive any sodium hydroxide. Treatments 5 and 6 were adjusted to pH 11.0 and 12.0, respectively, with NaOH (Table 7).

^b pH_{sol'n} = pH of groundwater prior to adding to sediment.

The aqueous chemical composition of selected solutions from the Fixed pH Experiment are presented in Tables 9 and 10. Table 9 describes the composition of treatment solutions prior to contact with sediment. Table 10 lists the composition of the treatment solutions after equilibrating with sediment for 14 days. As expected, the concentrations of sodium and carbonates increased with pH. The large increase in dissolved silica at pH ≥ 10.3 can be attributed to the dissolution of silicious minerals in the sediment. There were also rather large decreases in calcium and magnesium concentration as the pH was increased. As mentioned above, Treatments 5 and 6 showed evidence of precipitation. Once sediments were introduced into Treatments 1, 5, and 6, concentrations of dissolved U(VI) and magnesium decreased, and concentrations of dissolved silica increased (Tables 9 and 10).

Solubility and chemical speciation calculations were conducted using the geochemical equilibrium MINTEQA2 code (Version 3.10, [24]). This code contains the U thermodynamic constants of Wanner and Forest [25], consisting of 60 dissolved and 139 solid U species. The U(VI) speciation of the various NaOH-amended solutions were calculated. Additionally, the saturation index was determined to assist in identifying the likely mineral phases that may have precipitated during the equilibration period. The saturation index compares the appropriate ion activity products (IAP, the product of the molar activities of each reactant and product raised to its stoichiometric power) with the corresponding formation constant (K). The saturation index is the logarithmic ratio of the IAP and K:

$$\text{Saturation index} = \log \left(\frac{\text{IAP}}{\text{K}} \right). \quad (3)$$

The saturation index for a particular mineral is negative if the system is undersaturated with respect to that mineral. Conversely, the saturation index for a particular mineral is positive if the system is oversaturated with respect to that mineral.

The input data for these calculations are presented in Tables 9 and 10. All dissolved uranyl species were calculated to exist as neutral and anionic species (Table 11). In the five lowest NaOH treatment solutions (Treatments 1 to 5, pH 8.3 to 10.3), the carbonate-uranyl complexes were dominant. In the highest NaOH treatment solution (Treatment 6, pH 11.8), all dissolved U(VI) existed as hydroxide complexes. This change in speciation occurred because, as the pH increased, the number of moles of hydroxides also increased and these hydroxides were able to out compete the carbonate molecules to form uranyl complexes. The U(VI) speciation before and after equilibration with the sediment did not change greatly for Treatment 1 (pH 8.5) and Treatment 6 (pH 11.8) (Table 11). For

Table 10. Aqueous chemical composition (mg/L) of groundwater solutions spiked with U(VI) after equilibration with Trench AE-3 sediment: Stabilized pH Experiment

	Trt. 1 ^a	Trt. 2	Trt. 3	Trt. 4	Trt. 5	Trt. 6	(+) Control ^b	(-) Control ^b
pH _{sol'n} ^c	8.3	9.0	9.5	10.0	11.0	12.0	8.4	8.3
pH _{sol'n+sed.} ^c	8.5	8.3	8.4	9.1	10.3	11.8	8.6	8.3
UO ₂ ²⁺	0.117	0.102	0.104	0.088	0.017	0.0009	0.191	0.006
Cl ⁻	51	58	45	40	43	40	31	34
SO ₄ ²⁻	110	128	114	115	114	115	75	109
PO ₄ ³⁻	0.7	0.9	0.9	0.9	1.3	1.2	0.7	0.8
CO ₃ ²⁻	122	107	123	144	194	358	82	123
Ca ²⁺	76	37	20	6	2	4	59	74
K ⁺	21	28	16	9	5	7	37	13
Mg ²⁺	14.7	8.9	4.8	1.1	0.1	<0.1	17	14
Na ⁺	35	93	126	160	205	539	31	34
H ₄ SiO ₄ ⁰	71	71	67	61	100	449	57	73

^a Treatments are numbered in order of the increasing amounts of sodium hydroxide added to the groundwater. Treatment Number 1 received no sodium hydroxide.

^b (+) Control = no sediment + $\sim 190 \mu\text{g/L}$ UO₂²⁺ spike (-) Control = no spike + no sediment.

^c pH_{sol'n} = pH of groundwater prior to adding to sediment. pH_{sol'n+sed.} = pH of sediment/groundwater suspension at the end of the experiment.

Table 11. Results of thermodynamic calculations of U(VI) speciation in a groundwater before and after equilibration with Trench AE-3 sediment: Stabilized pH Experiment*

	pH	$\text{UO}_2(\text{CO}_3)_2^{2-}$ (%)	$\text{UO}_2(\text{CO}_3)_3^{4-}$ (%)	$\text{UO}_2(\text{OH})_2^0$ (%)	$\text{UO}_2(\text{OH})_3^-$ (%)	$\text{UO}_2(\text{OH})_4^{2-}$ (%)
Trt. 1 after sediment	8.5	23	75	1	—	—
Trt. 2 after sediment	8.3	35	62	2	—	—
Trt. 3 after sediment	8.4	28	70	2	—	—
Trt. 4 after sediment	9.1	7	93	—	—	—
Trt. 5 after sediment	10.3	—	98	—	2	—
Trt. after sediment	11.8	—	—	4	94	2
(+) Control ^(b)	8.6	27	68	3	2	—
(-) Control ^(b)	8.3	32	66	2	—	—
Trt. 1 before sediment	8.3	28	71	—	—	—
Trt. 5 before sediment	11	—	60	—	40	—
Trt. 6 before sediment	12	—	2	—	96	2

* Solution chemistry used in these calculation are presented in Tables 9 and 10. Treatments are numbered in order of the increasing amounts of sodium hydroxide added to the groundwater. Treatment Number 1 received no sodium hydroxide. Uranyl thermodynamic constants from Wanner and Forest (1992); MINTEQA2 software used to make thermodynamic calculations (Version 3.10, Allison *et al.* 1991). Only those species with concentrations >1% are included in this table, hence the sum of U(VI) species for any given solution may not equal 100%.

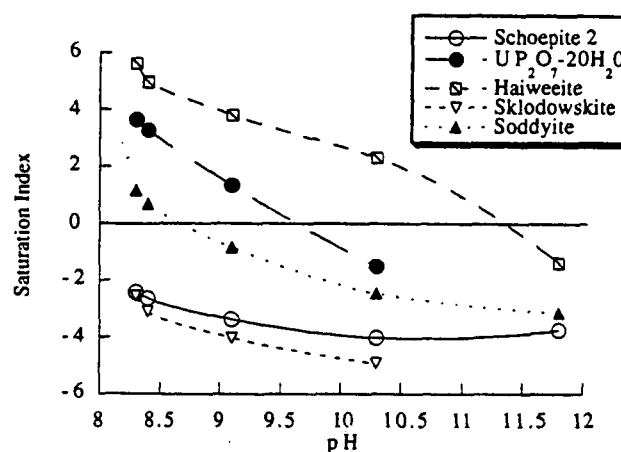
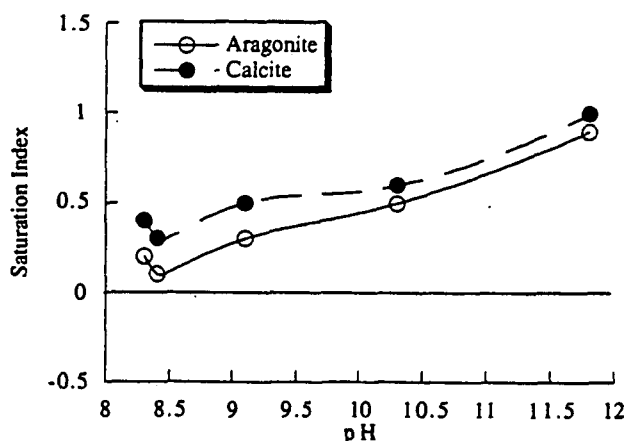
^(b) (+) Control = no sediment + ~190 $\mu\text{g/L}$ U(VI) (as UO_2^{2+}) spike. (-) Control = no spike + no sediment.

Treatment 5 (pH 10.3), more carbonate-uranyl species were observed after equilibration with the sediment. This difference may partially be attributed to the pH decrease from 11.00 (Table 7) to 10.27 (Table 8) during the 14-day equilibration period with the sediment.

The solution chemistry input values for the saturation indices calculations [Eq. (3)] included the initial U(VI) concentrations measured prior to contact with the sediment (Table 7), and the final pH, Cl^- , SO_4^{2-} , PO_4^{3-} , CO_3^{2-} , Ca, Mg, K, Na, and H_4SiO_4^0 concentrations of the treatment solutions after equilibration with the sediment (Table 10). Important mineral phases with saturation indices greater than zero (i.e., the solution is oversaturated with respect to that mineral) are presented in Figs. 3 and 4. The chemical compositions of these phases are:

Aragonite:	CaCO_3 (orthorhombic crystal structure)
Calcite:	CaCO_3 (hex/rhombo crystal structure)
Haiweeite:	$\text{Ca}(\text{UO}_2)_2\text{Si}_6\text{O}_{15} \cdot 5 \text{H}_2\text{O}$
Schoepite:	$\text{UO}_3 \cdot 2 \text{H}_2\text{O}$
Sklokovskite:	$\text{Mg}(\text{UO}_2)_2\text{Si}_2\text{O}_7 \cdot 4 \text{H}_2\text{O}$
Soddyite:	$(\text{UO}_2)_3\text{Si}_2\text{O}_9 \cdot 6 \text{H}_2\text{O}$

Some phases calculated to have saturation indices greater than zero are not included in Figs. 3 and 4 because they are either high temperature phases or are known to require more than 14 days to form under ambient conditions [e.g., CaUO_4 and wollastonite (CaSiO_3)]. Carroll and Bruno [18] reported the formation of rutherfordine (UO_2CO_3) when calcite was combined with U(VI) at concentration appreciably greater than those used in this study, $10^{-4.4}$ to $10^{-2.9}$ M. In this study, rutherfordine had a highly negative saturation index, suggesting it would not precipitate under these experimental conditions.

**Fig. 3.** Saturation indices for the most saturated uranium(VI) phases: Stabilized pH Experiment.**Fig. 4.** Saturation indices of calcite and aragonite: Stabilized pH Experiment.

Based on the data in these two figures, there appears to be at least two possible mechanisms for the precipitation of U(VI) from the high pH treatments in this experiment: 1) coprecipitation with calcite and aragonite, and 2) precipitation as a uranium phase. The phases with saturation indices greater than zero for Treatments 5 (pH 10.3) or 6 (pH 11.8) were aragonite, calcite, and halite.

An important distinction between the saturation indices of the uranium phases and the calcium carbonate phases is that the trend of the latter increased with pH, thus being more consistent with the experimental observations. Carbonate minerals, particularly aragonite, can incorporate several ppm U into their structure [26, 27]. Of the two calcium carbonate phases, aragonite is the more likely phase formed in this experiment because its rate of formation is faster than that of calcite [28, 29]. Over a period of years, aragonite commonly transforms in nature into calcite [29].

Conclusions

Uranium(VI) sorption in carbonate-containing groundwater and sediment systems is generally quite low due to the formation of anionic carbonate-uranyl complexes or neutral and anionic hydroxide-uranyl complexes. These complexes presumably tend to sorb appreciably less to sediments than cationic uranyl cations. This study evaluated the effect of elevated ionic strength and pH on U(VI) sorption to carbonate-containing sediments. The data show that U(VI) adsorption remained constant between the U(VI) solution concentrations of 3.3 and 100 $\mu\text{g/L}$, suggesting that the simple distribution coefficient (K_d) model could be used to describe adsorption for this system (pH 8.3, 0.02 M). Uranium(VI)- K_d values and solubility did not change as the ionic strength was increased to 14 mM with NaClO_4 . Uranium(VI)- K_d values increased from 1.07 to 2.22 mL/g as the pH of the system increased from pH 8.17 (ambient levels) to pH 9.31. At a pH ≥ 10.3 , precipitation and/or coprecipitation of U(VI) occurred, resulting in apparent K_d values > 400 mL/g. Precipitation did not occur unless a sediment was present, suggesting that precipitation reactions were heterogeneous in nature. The solid phase that containing the U(VI) precipitate was not identified directly. However, based on solubility calculations and consideration of U(VI) and calcium carbonate geochemistry and crystallography, it appears possible that the U(VI) coprecipitated with a calcium carbonate phase and was not precipitated as a separate U(VI) phase. Thus, in carbonate systems with a pH greater than approximately 10.5, U(VI) mobility may be much less than in near-neutral pH systems. These results have important ramifications for performance- and risk-assessment calculations involving the transport of U(VI) from highly alkaline sources, such as many types of tank waste and vitrified-, grout-, and saltstone-waste forms.

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